

# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION 10

1200 Sixth Avenue, Suite 900 Seattle, WA 98101-3140

OFFICE OF WATER AND WATERSHEDS

August 19, 2016

Brock Tabor Alaska Department of Environmental Conservation P.O. Box 111800 410 Willoughby Ave., Ste. 303 Juneau, AK 99811-1800

Re: Comments and Reponses Regarding the Draft Proposed Site Specific Criteria for the Chuitna Basin

Dear Mr. Tabor:

This letter summarizes comments and responses regarding ADEC's July 2014 draft site-specific criteria (SSC) for the Chuitna mine site that are still under discussion between EPA and ADEC. The draft SSC included aquatic life criteria for copper, aluminum, and zinc, and a human health criterion for manganese. ADEC recently informed EPA that PacRim Coal, LP (PRC, the applicant) is not pursuing SSC for aluminum and zinc at this time. Comments regarding the aluminum and zinc SSC are also summarized below to document their status in case the applicant and ADEC wish to pursue these SSC in the future.

## A. Representativeness and Protectiveness of the Draft Aquatic Life SSC

The temporal and spatial representativeness of location 141 relative to the entire SSC site has been a central discussion point since the SSC development work was in its planning stages. EPA commented on the draft decision document that "...DEC has not supplied adequate evidence that Station 141 reflects the full temporal and spatial variability of the water chemistry in the watershed" (EPA 2014b, p. 2). Although ADEC and the applicant have provided several documents that include descriptive statistical representations of many of the parameters that affect metals bioavailability, an inferential statistical evaluation focused on these parameters was not provided. EPA's analysis (EPA 2016c; attachment C) showed temporal and spatial variability in factors that affect metals toxicity, as discussed below. Additionally, to fully protect the aquatic life use, any SSC must be protective under the full range of conditions that occur at the site, including conditions of high metals bioavailability and toxicity (i.e., "sensitive conditions"). The range of conditions at the Chuitna mine site is discussed below in section C relative to the draft aluminum SSC. The methods used and conclusions of that discussion would also be relevant for development of SSC for other pollutants where bioavailability varies with changes in water chemistry, including copper and zinc.

EPA also commented that metal bioavailability factors in any lakes and wetlands that are part of the site to which the SSC apply have not been evaluated (EPA 2015b, first general comment). ADEC (2015) indicated that the SSC will only apply to the streams themselves, not to areas outside of the stream channels, and that lakes and wetlands are located upstream of the stream channels, with the exception of two wetlands in the Lone Creek channel. During a subsequent conference call, the agencies and the applicant discussed the possibility of using data for the

nearest downstream sampling location to evaluate wetlands in the Lone Creek basin, and this approach could be evaluated further. However, Lone Creek is no longer part of the site for the copper SSC, which currently only encompasses Middle Creek, and this comment may not be applicable to the waters of Middle Creek. In any event, any waters that are part of the SSC site and that may reasonably be expected to differ in chemical composition from stream water would need to be accounted for in the development of SSC. Downstream protection standards would apply to waters that are outside of the site but are adjacent to or downstream of site waters.

## **B.** Copper SSC

To evaluate whether the draft copper SSC were protective of the aquatic life use, including during conditions of high copper bioavailability, EPA completed two analyses (EPA 2014b):

1. A comparison of DOC levels in the water effect ratio (WER) samples to the range of (estimated) DOC concentrations at the site, and 2. A comparison of the draft WER-based SSC to criteria calculated using the biotic ligand model (BLM; EPA 2007). Based on these analyses, EPA found that the draft copper SSC would not be protective, particularly during conditions of high copper bioavailability. Following subsequent discussions between the agencies and the applicant, PRC evaluated the feasibility of using the BLM to develop SSC (PRC 2015) and began developing procedures for establishing model inputs for missing data (PRC 2016 and Tetra Tech 2016b). The use of the BLM was discussed by the agencies and the applicant during a conference call on April 7, 2016, and EPA subsequently provided a summary of its BLM analysis to ADEC and the applicant (EPA 2016a; attachment A).

EPA appreciates ADEC's and PRC's efforts to develop BLM-based SSC for the Chuitna site and looks forward to additional discussion regarding the use of the model.

#### C. Aluminum SSC

ADEC's draft decision document for the Chuitna SSC included a site-specific chronic criterion for aluminum that was derived as the geometric mean of three WER tests, which were completed in October and November 2009 using samples collected from location 141. EPA provided comments on December 12, 2014 and March 25, 2015 regarding the representativeness of these tests and the protectiveness of the derived criteria (EPA 2014b, 2015b). In summary, EPA commented that the high variability of the aluminum WERs was not adequately explained; that characterizing the entire site using samples collected from one location was not sufficient; and that the use of a geometric mean to determine a final WER may result in a criterion that is not protective for all conditions.

ADEC's response to comments (ADEC 2015) summarized the initial planning process for the Chuitna WER development project, including data evaluations that had been completed to support the selection of location 141 for the WER tests, and also noted the low toxicity of aluminum in water at pH values close to 7, citing difficulties of toxicity testing related to aluminum solubility and variable toxicity test data found in the literature. ADEC (2015) reiterated the position that the final WER should be determined as the geometric mean of the individual WERs, stating that "all of the flow conditions tested occur frequently in this system and are therefore equally important to aquatic life." EPA continues to disagree with this conclusion as discussed further below, because the criteria must protect aquatic life under the

range of conditions that occur at the site, including conditions of high metals bioavailability and toxicity.

Following conference calls between ADEC and EPA in 2015, ADEC requested additional information from PRC to address EPA comments (ADEC 2016). As part of its response, PRC reduced the extent of the site for the aluminum SSC to include only Middle Creek and the Chuitna from Middle Creek to its mouth at Cook Inlet with the goal of addressing EPA's concerns about the variability of toxicity-mitigating factors at the site (PRC 2016 and subsequent conversations between ADEC and EPA). ADEC provided two additional memoranda to EPA regarding the variability of aluminum toxicity factors at the site (TetraTech 2016a,c), which were discussed during conference calls between the agencies and PRC on March 21 and April 1, 2016. EPA provided comments on the Tetra Tech memoranda and on a third memorandum (Tetra Tech 2014) regarding variability of toxicity-mitigating factors at the site in a July 21, 2016 technical memorandum (EPA 2016c), which is included in this letter in attachment C. EPA also completed an analysis of data for metals toxicity-mitigating factors at the mine site and found statistically significant spatial and temporal variations (EPA 2016c).

EPA provided comments regarding the WER results, toxicity testing procedures, and a comparison of the draft Chuitna SSC to recent peer reviewed and published aluminum toxicity data during the April 1, 2016 call. This information was summarized in a June 24, 2016 memorandum (EPA 2016b), which is included in attachment B.

EPA's memoranda provide options for ADEC to consider when developing SSC for aluminum, which include the use of a peer-reviewed BLM or multiple linear regression model for aluminum (EPA 2016b), adopting EPA's draft 304(a) criteria when available (EPA 2016b), or completing additional WER tests that capture sensitive conditions and incorporate best practices for aluminum toxicity testing to minimize aluminum solubility issues (EPA 2016c). Any of these approaches could be used to generate a chronic aluminum SSC; however, the final criterion must protect sensitive conditions as well as typical conditions, regardless of the approach that is used to develop the SSC.

EPA recognizes that ADEC is not pursuing SSC for aluminum and zinc at this time and provides the above summary to document communications and clarify EPA's position in the event that ADEC wishes to pursue aluminum SSC at a future time.

## D. Considering Sensitive Species in Developing Aluminum SSC

EPA (2014b) commented that "EPA has concerns about the sensitivity of salmonids to aluminum, potentially both at the site and downstream of the site" and that "downstream impacts from the site due to aluminum, and other metals, on salmonids and other taxa should be considered." EPA's guidelines for deriving aquatic life criteria provide generally for the protection of aquatic communities and specifically for the protection of "commercially, recreationally, and other important species" (Stephen et al., 1985, p. 2). The guidelines include procedures for lowering the acute and chronic criteria to accommodate important species, stating for acute criteria: "if the Species Mean Acute Value of a commercially or recreationally important species is lower than the calculated Final Acute Value, then that Species Mean Acute Value replaces the calculated Final Acute Value in order to provide protection for that important

species" (Stephen et al., 1985, p. 14). Chronic criteria are addressed similarly for important species: "[I]f the Species Mean Chronic Value of a commercially or recreationally important species is lower than the calculated Final Chronic Value, then that Species Mean Chronic Value should be used as the Final Chronic Value instead of the calculated Final Chronic Value" (Stephen et al., 1985, p. 22). A large body of peer-reviewed toxicity data has been published since EPA published its 304(a) criteria for aluminum in 1988. Any aluminum SSC generated for the Chuitna mine site should be evaluated against the current toxicity literature to ensure that the SSC are protective of salmon and other commercially and recreationally important species in the waters to which the SSC will apply, and downstream of those waters.

Any criteria must also be protective of Endangered Species Act (ESA)-listed threatened and endangered species and designated critical habitat present at the site, including listed species and critical habitat downstream of the site to which the criteria would apply. This related topic is discussed below in section J.

#### E. Zinc SSC

ADEC has indicated that it is no longer planning to adopt SSC for zinc at this time. The following information is provided to document the status of EPA's comments regarding the zinc WERs and SSC, in the event that SSC for zinc are developed for the Chuitna mine site in the future.

EPA (2014b, comment A.III) noted that two of the three zinc WERs were close to 1, and that the WER test results would therefore not justify an increase in the zinc criteria above Alaska's current criteria. EPA (2015b) also commented that the WER samples did not capture the range of spatial and temporal variability at the site. ADEC reduced the extent of the site for the zinc SSC to include only Middle Creek to its confluence with the Chuitna (PRC 2016) in response to these comments, but ADEC has not demonstrated that the existing WER samples represent sensitive conditions found in this reduced site.

The EPA comment regarding the magnitude of the WERs has also not been addressed. PRC (2016) discussed the use of a geometric mean in connection with the aluminum WERs, generally citing EPA WER guidance as recommending this approach. For Method 1, EPA's WER guidance recommends use of the geometric mean for individual WERs that are derived for similar conditions, and the geometric mean of these individual WERs is used as the final WER when the individual WERs represent the most sensitive conditions (EPA 1994, pages 35 - 36). Overall, EPA (1994) requires SSC to be protective of the range of conditions at a site, including sensitive conditions. SSC based on the geometric mean of the three zinc WERs, which reflect different flows, would not be protective of sensitive conditions at the site.

#### F. Metals Mixture Test

ADEC has indicated that it is no longer planning to adopt SSC for aluminum and zinc at this time, and that the BLM will be used to develop SSC for copper. Several of EPA's comments addressed the metals mixture tests that were completed as part of the SSC development process (EPA 2014b, section A.V), stating that 1) The sample used for metals mixture tests had high hardness, DOC, and TSS levels that may have resulted in low metals toxicity overall relative to

typical conditions, and 2) The statistical methods used to evaluate toxicity may not have been appropriate. If WER-based SSC are developed in the future, these comments would need to be addressed.

# G. Addressing Future Changes in Water Quality

Comment VII.2 of EPA (2014b) stated that because of lower TOC levels and pH in groundwater at the site relative to surface water, groundwater discharged into the streams may increase the toxicity of metals at the site. EPA is concerned that WER- or BLM-based SSC developed under current conditions may no longer be protective once the mine effluent is discharged, as the effluent would likely change the concentrations of toxicity mitigating factors such as DOC and pH. The metals could be more toxic under post-effluent conditions than they are under current, pre-effluent conditions. They could also be less toxic, depending on specific conditions; for example, high conductivity noted in groundwater from several hydrostratigraphic units reflects high ion content, which would mitigate copper toxicity.

ADEC indicated in its response to EPA's comments (ADEC 2015) that the mine effluent would be addressed during permitting and should not be addressed as part of the SSC development process. The comment response provided a description of the process by which the permitting program could address potential toxicity issues related to a mine discharge, including monitoring and whole effluent toxicity (WET) testing in addition to the permit limits themselves. ADEC also indicated that an antidegradation analysis would be required as part of the permitting process and would provide additional protection.

Following discussions between ADEC and EPA regarding this comment and the need to ensure the continuing relevance of the SSC in addition to demonstrating that the effluent was not toxic, ADEC proposed to include minimum "trigger" levels for DOC, pH, and hardness as part of the copper SSC. Discussions about this approach are ongoing between ADEC and EPA. Post-discharge conditions should also be considered for development of any other SSC for the site. EPA looks forward to additional discussion with ADEC regarding future relevance of the copper SSC as part of the development of the BLM-based copper SSC and their implementation procedures for the Chuitna site (see section B above).

#### H. Downstream Protection

ADEC's draft decision document for the Chuitna SSC included a discussion of downstream protectiveness of the proposed criteria and referenced a loading analysis completed by PRC (TetraTech 2013) to evaluate the protectiveness of the criteria. EPA provided comments on this loading analysis on January 8, 2015 (EPA 2015a), which were partially resolved by ADEC's response to comments (ADEC 2015; comments D1 and D4 are resolved). However, two of EPA's comments (EPA 2015a and ADEC 2015, comments D3 and D4) warrant further consideration, particularly in light of EPA's recent guidance related to downstream protection (EPA 2014a).

EPA commented that the assumption of a 50% dilution at the point of discharge was not consistent with the purpose of the downstream analysis, which is to evaluate the effect of metals at the SSC concentration on the downstream waters of the Chuitna. By assuming a 50% dilution,

the loading analysis evaluated downstream impacts for metals at half the proposed SSC, rather than the full value of the SSC. EPA (2015a) stated: "the tributary metal concentrations should be set to the SSC values, not flow-adjusted values" and "ADEC's approach to the loading analysis would be consistent with a NPDES permit that does not allow a mixing zone. In this case, the effluent would meet the SSC at the point of discharge and the receiving water would in effect dilute the discharge to a level below the SSC." In its May 2015 response, ADEC disagreed with EPA's comment, stating: "It would be unrealistic to assume a loading application that is inconsistent with ambient site water quality in order to perform a reasonable assessment of downstream loading effects."

EPA (2015a) also commented that the data used to evaluate downstream protection did not address flows with return periods less than 1 to 2 years, and therefore did not "approximate the 'frequency of exceedance' component of the SSC." ADEC (2015) responded that "the performed loading analysis generally followed methods outlined by EPA's Technical Support Document for Water Quality-Based Toxics Control" and that "low flows have 'traditionally' been used and accepted for calculation of the TMDLs, evaluation of mixing zones, and long-term water quality assessments."

EPA's comments on the downstream analysis and ADEC's responses appear to address different objectives. A loading analysis would be used to evaluate potential downstream effects of a permitted discharge. ADEC's response is consistent with a loading analysis to support a permit level, but for development of SSC, EPA's concern is that the SSC themselves do not result in a violation of downstream water quality criteria, and not whether a specific effluent will meet downstream criteria. EPA acknowledges ADEC's responses to the two unresolved comments and provides the following general background regarding downstream protection in water quality standards (WQS) and specific considerations for developing SSC for the Chuitna site that also protect downstream waters.

40 CFR 131.10(b) provides that "[i]n designating uses of a water body and the appropriate criteria for those uses, the state shall take into consideration the water quality standards of downstream waters and ensure that its water quality standards provide for the attainment and maintenance of the water quality standards of downstream waters." States and authorized tribes generally have discretion in choosing an approach to downstream protection based on individual circumstances; such an approach may include adoption of narrative criteria, numeric criteria or a combination of the two. EPA's guidance suggests that states and tribes should consider a tailored and specific narrative criterion and/or numeric criteria in certain situations, such as when more stringent numeric criteria are in place downstream and/or environmental justice (EJ) issues are relevant (EPA 2014a, p.4).

EPA's guidance (EPA 2014a) suggest several ways by which states can develop narrative and/or numeric upstream standards to ensure attainment and maintenance of downstream standards. If a state or tribe opts to pursue adoption of numeric criteria to ensure downstream protection, EPA (2014a) notes the use of water quality modeling applications to assist in identifying appropriate numeric criteria as one approach to consider. Other possible approaches include using the downstream criteria as the applicable criteria at the pour point of the upstream tributary into the downstream water body, or using regression to relate downstream pollutant concentrations to upstream concentrations (EPA 2014a, p. 10). The approaches described in the guidance are not

exhaustive and states and authorized tribes have certain discretion in choosing a preferred approach, depending on the circumstances, as long as the resulting criteria ensure the attainment and maintenance of downstream WQS (EPA 2014a, pp. 5, 6, 8, 9 and 10).

Another option for ensuring that SSC at the Chuitna site provide for the attainment of downstream criteria is to adopt a downstream protection value (DPV) that is the same as the criteria for the downstream water. EPA (2014a) describes DPVs as "numeric water quality criteria (with magnitude, duration, and frequency), developed in tandem with upstream criteria and designated uses, which are derived to ensure attainment and maintenance of downstream WQS." EPA (2014a) further states that DPVs may be established at strategic locations, including "the mouths of specific tributaries to estuaries, lakes or rivers, or other locations where numeric water quality criteria may be key to efficiently protecting downstream water quality through effective management decisions upstream (e.g., derivation of effluent limitations, via modeling, to prevent exceedance of the DPV)." The mouth of Middle Creek, its pour point to the Chuitna, would be a logical place to establish a DPV. The pour point criteria would reflect the hardness-based criteria of the receiving water for copper. EPA recommends that ADEC adopt a DPV as part of its SSC for Chuitna, or develop another approach to ensure the attainment and maintenance of downstream WQS as described in EPA (2014a).

#### I. Tribal Considerations

EPA (2015b) commented that in acting on a state WQS submittal, it must ensure that the WQS comply with the Clean Water Act (CWA) and all other applicable laws. This may include laws that apply to tribal resources, such as reserved fishing rights found in treaties, court cases, and federal statutes (e.g., land claim settlement acts). ADEC (2015) responded that the Alaska Attorney General's Office had indicated that ADEC has sole environmental regulatory jurisdiction because the Alaska Native Claims Settlement Act has extinguished all aboriginal fishing rights held by Alaska tribes. EPA has shared with ADEC that EPA has received requests from the Native Village of Tyonek and committed to offer government-to-government consultation prior to EPA taking formal CWA action on a final SSC for the Chuitna site. EPA continues to recommend that ADEC conduct its own tribal outreach on the draft SSC (specifically to the Native Village of Tyonek) and more generally on other proposed water quality standards revisions to ensure that tribal input is fully considered.

#### J. ESA Consultation Considerations

EPA indicated in its March 25, 2015 comments that additional considerations regarding the proposed SSC may arise as a result of consultation under the Endangered Species Act (ESA). EPA would consult with the National Marine Fisheries Service (NMFS) and the U.S. Fish and Wildlife Service (FWS) as required on an approval action on SSC that are submitted for review under section 303(c) of the CWA. ADEC has indicated an interest in taking part in any ESA consultation as an applicant (ADEC 2015).

To meet requirements of the ESA, any SSC that EPA formally approves must not jeopardize threatened or endangered species or result in destruction or adverse modification of critical habitat (ESA Section 7 part 2). The following information is provided in consideration of this

requirement. EPA initially provided most of this information during our call with ADEC and PRC on April 1, 2016, prior to ADEC's withdrawal of the aluminum and zinc SSC.

Four endangered species managed by NMFS occur in Cook Inlet, as follows:

Species	Occurrence	Diet	Citation
Steller sea lion	Regular	variety of fishes (capelin, cod,	http://www.fisheries.no
(Eumetopias		herring, mackerel, pollock,	aa.gov/pr/species/mam
jubatus) Western		rockfish, salmon, sand lance, etc.),	mals/sealions/steller-
DPS		bivalves, squid, octopus, and	sea-lion.html
		gastropods	
Cook Inlet	Regular	opportunistic feeders, belugas eat	http://www.fisheries.no
beluga whale		invertebrates such as octopus,	aa.gov/pr/species/mam
(Delphinapterus		squid, crabs, shrimp, clams,	mals/whales/beluga-
leucas) and its		mussels, snails, sandworms, and a	whale.html
critical habitat		variety of fishes including salmon,	
		eulachon, cod, and, flounder	
Fin whale	Regular	krill, small schooling fish (e.g.,	http://www.fisheries.no
(Balaenoptera		herring, capelin, and sand lance),	aa.gov/pr/species/mam
physalus)		and squid; they fast in the winter	mals/whales/fin-
		-	whale.html
Humpback	Regular	tiny crustaceans (mostly krill),	http://www.fisheries.no
whale		plankton, and small fish; they can	aa.gov/pr/species/mam
(Megaptera		consume up to 3,000 pounds of	mals/whales/humpback
novaeangliae)		food per day	-whale.html

These species feed on small fish, including salmonids, which are among the most sensitive species to aluminum and copper. Effects of the SSC on listed species and designated critical habitat, including availability of and toxicity to prey species, are expected to be addressed during any ESA consultation.

While salmonids are not listed under the ESA in Alaska, Chinook salmon are listed as Alaska Stocks of Concern by the Alaska Department of Fish and Game:<sup>2</sup>

System	Species	Area	Year	Level of	Year Last
			Designated	Concern	Reviewed
Chuitna	Chinook	Cook Inlet	2010	Management	2010
River					

In the event that EPA would need to consult on federally designated critical habitat for the Cook Inlet beluga whale, EPA would need to evaluate potential effects on specific prey species, including four species of Pacific salmon, to ensure that designated critical habitat is protected.

<sup>2</sup> http://www.adfg.alaska.gov/index.cfm?adfg=specialstatus.akfishstocks, accessed 3/3/16

<sup>&</sup>lt;sup>1</sup> https://alaskafisheries.noaa.gov/sites/default/files/ak specieslst.pdf, accessed 3/31/16

EPA appreciates ADEC's and PRC's work in preparing the draft SSC and we look forward to continued discussions on the BLM-based copper SSC and review of the revised SSC and decision document.

Sincerely,

Maja Tritt

Water Quality Standards Coordinator

Attachments

#### References

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- ADEC 2016. Technical Memorandum. Chuitna Coal Project Site Specific Criteria. February 4, 2016.
- EPA 1994. Interim Guidance on Determination and Use of Water-Effect Ratios for Metals. EPA Office of Water, Washington, DC and EPA Office of Research and Development, Duluth, MN and Narragansett, RI. February 1994.
- EPA 2014a. Protection of Downstream Waters in Water Quality Standards: Frequently Asked Questions. EPA-820-F-14-001. EPA Office of Water, Washington, DC. June 2014.
- EPA 2014b. EPA's Comments on Draft Proposed Site Specific Criteria and Seasonal Use Revision for Chuit River and Three Tributaries. EPA Region 10, Seattle, WA. December 12, 2014.
- EPA 2015a. EPA's Comments on Draft Proposed Site Specific Criteria for Chuit River and Three Tributaries: Loading Analysis for Downstream Protection. EPA Region 10, Seattle, WA. January 8, 2015.
- EPA 2015b. EPA's Supplemental Comments on Draft Proposed Site Specific Criteria and Seasonal Use Revision for Chuit River and Three Tributaries. EPA Region 10, Seattle, WA. March 25, 2015.
- EPA 2016a. Technical memorandum. EPA's Input Data for Copper BLM Evaluation for the Chuitna Site. May 31, 2016.
- EPA 2016b. Technical memorandum. Summary of EPA's Discussion Points Regarding Aluminum Toxicity and WER Testing Presented on an April 1, 2016 Call with ADEC and PacRim. June 24, 2016.
- EPA 2016c. Technical memorandum. Variability of Factors that Affect Aluminum Toxicity at the Chuitna Site and Considerations for WER-Based Site-Specific Criteria Development. July 21, 2016.
- PRC 2015. Chuitna Coal Project Site Specific Criteria for Copper, Confirmation of Hardness-based criteria from 2009 WER using BLM calculations. December 9, 2015.
- PRC 2016. Letter to Brock Tabor Re: Responses to Feb 3, 2016 SSC Comments from ADEC and the USEPA. February 29, 2016 (letter is misdated January 29, 2016).
- Stephen, Charles E., Donald I. Mount, David J. Hansen, John R. Gentile, Gary A. Chapman, and William A. Brungs. 1985. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses. PB85-227049. EPA Office of Research and Development, Duluth MN, Narragansett, RI, and Corvallis, OR. 1985.
- TetraTech 2013. Technical Memorandum. Loading Analysis. December 17, 2013.

- Tetra Tech 2014. Draft Technical Memorandum. Results of Studies to Establish Site Specific Water Quality Criteria for Aluminum in the Chuit River. February 27, 2014.
- Tetra Tech 2016a. Technical Memorandum. Critical Stream Conditions for Aluminum Toxicity and WER Sampling. March 16, 2016.
- Tetra Tech 2016b. Memorandum. BLM Analysis. March 18, 2016.
- Tetra Tech 2016c. Technical Memorandum. Regression Analysis between Various Parameters Stream 2003 Surface Waters. April 12, 2016.





# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION 10

1200 Sixth Avenue, Suite 900 Seattle, WA 98101-3140

OFFICE OF WATER AND WATERSHEDS

# **MEMORANDUM**

**TO:** Brock Tabor

Alaska Department of Environmental Conservation

**FROM:** Maja Tritt

**DATE:** May 31, 2016

**SUBJECT:** EPA's Input Data for Copper BLM Evaluation for the Chuitna Site

During our call on April 7, 2016, ADEC, PacRim Coal, and EPA discussed the biotic ligand model (BLM) evaluations that EPA and PacRim each prepared for the Chuitna site in connection with the development of site-specific criteria (SSC) for freshwater copper. ADEC provided its evaluation to EPA on March 18, 2016 (memo from Jerry Diamond and Marcus Bowersox, Tetra Tech, to Dan Graham, PacRim Coal, dated March 18, 2016) and requested EPA's copper BLM analysis for the Chuitna site during our April 7 call. EPA is providing the attached spreadsheet in response to this request. Please note that EPA compiled the BLM input data from available site data (see below) and estimated input values when data were not available, as described below. The methods EPA used to estimate input parameters can be used with the BLM to gain a general sense of the range of instantaneous water quality criteria (IWQC) at the site. However, EPA would not necessarily consider the methods appropriate for developing SSC. In particular, because copper toxicity and BLM predictions are highly sensitive to DOC concentrations, it is important to use representative site-specific measurements of DOC or develop a representative and protective DOC:TOC ratio to estimate DOC data when developing SSC.

The data in the BLM input data spreadsheet were taken from Appendix B16: *Historical Surface Water Quality Data* of the 2009 surface water baseline report. The methods EPA used to estimate missing BLM input parameters and clarifications regarding the relevance of these methods to SSC development are as follows:

1. To estimate dissolved organic carbon (DOC) from available total organic carbon (TOC) measurements, EPA used the most conservative (i.e., lowest) DOC:TOC ratio available from the water effects ratio (WER) study work (68%). Because only four measurements were available, collected in autumn (i.e., October and November, 2009 and December, 2010), all at one station on Middle Creek, neither the spatial nor the temporal variability of the potential ratios of DOC:TOC in the watershed were represented sufficiently to use a geometric mean of the

available ratios. The lowest available DOC:TOC ratio was therefore selected for the purpose of this analysis.

However, EPA does not consider the existing DOC data sufficient to establish a representative or protective DOC:TOC ratio for the entire site to which the proposed SSC would apply. Given the data limitations described above, additional data are necessary to better characterize DOC levels at the site, spatially and temporally. This could be accomplished by collecting additional paired DOC and TOC data to better characterize the DOC:TOC ratio. Alternatively, additional samples of all ten BLM input parameters (including DOC instead of TOC) could be collected, sufficient to capture both temporal and spatial variability at the site, and with consideration of downstream protection.

- 2. TOC data were missing in a few instances, and therefore EPA could not calculate corresponding DOC values. In these cases, EPA used the geometric mean of the available calculated DOC values at the site to estimate the missing DOC value. EPA used this approach at the following stations:
  - Chuit River C045, C120
  - Middle Creek Q170, C128, and C140

These estimated DOC values are shown in red font in the data tables.

3. In February 2007, very high TOC was observed across all stations. The TOC values varied between 20-40 mg/L, approximately 5-10X higher than the next highest TOC reading at any given site. EPA retained these high TOC values and used them in the IWQC calculations despite the uncertainty associated with these values as potential outliers.

Specifically, the following points are noted regarding the high TOC measurements in February, 2007:

- Given that the samples were taken in February, it would seem like this time was either before or close to the beginning of winter thaw, which could potentially explain higher TOC, however, samples taken a year later in February 2008 were not elevated when compared with the overall TOC dataset for each station.
- It's possible that the high values are elevated because of an analytical chemistry or database error.

EPA recommends review of these data, including laboratory documentation and database entries, to confirm absence of a traceable error or to correct the values. Given that the values, if correct, would appear to represent an unusual condition that occurs on an infrequent basis and is of short

duration, if these values were used to develop SSC, EPA would need to better understand the accuracy and reliability of these measurements.

- 4. The project database includes pH measurements completed in the field and at the laboratory. EPA used lab pH values because only one measurement of field pH was reported for each site. Field pH measurements are more reliable than lab measurements because pH can change rapidly once a sample is collected. As a general consideration, EPA strongly recommends collection of field pH measurements for use with the BLM.
- 5. Ions that were not detected were reported with a "<" symbol in the surface water baseline report. In this case, EPA used the full detection limit as the BLM input value. TetraTech (2016) appears to have used half the detection limit for non-detects, a slightly more conservative approach that is preferable for SSC development.
- 6. We assumed 10% humic acid (HA) as a conservative input because no site-specific data exist. The 30% HA described by PacRim is not based on data; rather it is an assumption based on the presence of peat soils in the Middle Creek watershed that are described as qualitatively similar to soils in the Kenai region, which were found to contain elevated levels of HA (Shoji et al. 1988 as cited in Tetra Tech 2016). Tetra Tech (2016) assumes these conditions are present in site soils and influence the %HA of the DOC in the waters in question. However, Tetra Tech (2016) does not include quantitative evidence to support these assumptions. Unless ADEC demonstrates that an alternative HA percentage is technically defensible based on fully representative quantitative data, EPA would use the 10% default HA value to evaluate protectiveness of the SSC.

All other chemistry data were used as reported in the spreadsheets.





# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION 10

1200 Sixth Avenue, Suite 900 Seattle, WA 98101-3140

OFFICE OF WATER AND WATERSHEDS

# **MEMORANDUM**

**SUBJECT:** Summary of EPA's Discussion Points Regarding Aluminum Toxicity and WER

Testing Presented on an April 1, 2016 Call with ADEC and PacRim

**FROM:** Maja Tritt

**TO:** Brock Tabor

Alaska Department of Environmental Conservation

**DATE:** June 24, 2016

During an April 1, 2016 call between EPA, ADEC, and PacRim regarding the Chuitna SSC for aluminum, PacRim requested a summary of EPA's discussion points regarding aluminum toxicity and the WER tests completed for the Chuitna site. The following information is provided in response to this request. Included are discussions of the WER toxicity test results and procedures; the magnitude of the proposed SSC relative to current data on aluminum toxicity; and special considerations for salmonids. These comments provide additional clarifications and considerations relative to comments that EPA provided to ADEC on 12/12/2014 and 3/25/1015 that have not been resolved following ADEC's response to comments (ADEC 2015) and subsequent conference calls between the agencies and with the applicant.

# I. WER Toxicity Tests

This section is related to comments A.II.1 and A.II.2 of EPA's 12/12/2014 comments, which address the variability of the WER test results for aluminum and the use of the geometric mean of the individual WERs to establish a final WER and develop the aluminum SSC. EPA recommended additional WER testing in its comments and provides recommendations for aluminum toxicity test procedures below. The following items were discussed during our April 1, 2016 call.

## 1. Magnitude and range of WERs

The interim WER guidance (EPA 1994, page 61) states, "If the WER is larger than 5, it should be investigated." Two of the three aluminum WERs were greater than 5, and further examination of these values is therefore warranted.

Furthermore, the 1994 WER guidance document on page 36 cautions the use of calculated WERs that differ by more than a factor of 5. The lowest WER result (2.68) differs by more than a factor of 5 from the highest WER result (22.0). As indicated in

Comment A.II.1 of EPA (12/12/2014), additional explanation is needed for the wide range of the reported WERs. The WERs may reflect variations in field conditions or in laboratory tests, and the source of the variation needs to be understood to ensure that an appropriate process is used to determine a protective final WER.

#### 2. Calculation of the final WER

As indicated in comment A.II.2 of EPA's 12/12/2014 comments on the Chuitna SSC, the selection of a final WER that is calculated as the geometric mean of the three rounds of testing is not appropriate. While the decision document (ADEC 7/5/2014) cites the 2001 guidance document as justification for this calculation, that document is a streamlined guidance document that applies only to copper and WWTPs and is not appropriate for an aluminum SSC.

From a practical standpoint, using a final WER that is the geometric mean of individual WERs representing different conditions results in the protection of only a portion of the tested conditions. In the case of aluminum, if the WERs accurately reflect conditions during different flow regimes, the final WER of 7.48 is greater than two of the three WERs reported for the site. If this value is used, then the site would only be clearly protected when the stream is at low flow conditions (Round 3 of testing with a WER of 22.0). SSC based on a geometric mean of the individual WERs would not protect aquatic species under medium and possibly high flow conditions.

# 3. Unexpected toxicity trends

The pH and DOC for each of the three WERs decreased while the LC50 values increased. This trend is the opposite of what would be expected based on how these parameters are known to affect aluminum bioavailability. It is also noted that hardness increased with increasing LC50, which is expected. However, hardness was only 2 mg/L higher in WER Test #3 than Test #2 while the LC50 increased 3.3 fold, whereas hardness increased by 4 mg/L from Test #1 to #2 with only a 1.4 fold increase in the LC50. These details suggest the presence of factors that may have interfered with the toxicity tests which have not yet been accounted for, but should be. The differences may be related to formation of aluminum floc, as described below.

## 4. Duration of toxicity tests

The duration of the aluminum toxicity tests was not consistent with current practice. 96 hour tests are generally used for acute toxicity tests with fish (Stephan et al. 1985) such as fathead minnow for aluminum, but 48 hour acute toxicity tests were used for the Chuitna WER tests, a duration more appropriate for short-lived organisms such as midges and cladocerans (Stephan et al. 1985).

The interim WER guidance (EPA 1994, p. 148) recommends the use of daphnid tests for aluminum, or tests used in the aluminum criteria document. Tests FM (recommended for zinc) and FX (recommended for silver) use fathead minnow, as described on p. 149. FM is a 48-hour test and FX is a 96-hour test.

According to standard protocol (ASTM 2014), fathead minnow tests should be of 96 hour duration. ASTM (2014) states:

# 11.7 Duration of Test

11.7.1 Whenever possible, the exposure duration should be sufficient to ensure that a time-independent toxicity level can be determined or estimated mathematically. In any case, daphnids and larvae of midges and phantom midges should be exposed to the test material for 48 h. All other species should be exposed for at least 96 h [emphasis added]. When renewal or flow-through tests are conducted with organisms that will not be substantially affected by starvation for at least 8 days, the test should last for at least 8 days to determine whether additional organisms are affected or killed after 96 h.

EPA recommends that any further aluminum toxicity tests with fish species are run for a duration of 96 hours, consistent with current protocols and practice. On our 4/1/2016 call, Tetra Tech stated that the WER would be the same irrespective of test duration. EPA requests detailed scientific information to substantiate this perspective.

#### 5. Use of static and static renewal tests

The interim WER guidance, item 5b of section G (page 51) describes renewal procedures required for WER tests. Tests must be renewed every 24 hours if the dissolved metal decreases by more than 50% over 48 hours.

The WER report (Tetra Tech 2010a, p. 14) states:

The first round of testing included sample renewal because metal concentration decrease was unknown. The second round also used renewals because the concentration change had not yet been quantified. Round 3 was not a renewal test as Rounds 1 and 2 did not have concentrations that decreased by more than 50% (EPA 1994).

The above may be correct, however, the WER report (page 14) does not provide sufficient detail (i.e., no concentration data at 24 and 48 hour time points) about changes in dissolved aluminum concentrations from the beginning to the end of the tests. No concentration information is provided for the third test. It is possible that the difference in renewal treatments contributed to the high variability of the three WERs.

#### 6. Stock solution versus direct aluminum salt addition to test water

The interim WER guidance, item 4 of section G (pages 50 - 51) requires use of the same aluminum stock solution for all tests and does not give the option to directly add the aluminum salt to the sample.

Page 14 of the WER report (Tetra Tech 2010a) states:

Aluminum added to solutions for use in testing was in the form of aluminum chloride hexahydrate (AlCl·6H20). Due to the high concentration of aluminum, a stock solution was not made prior to testing, rather the aluminum chloride was added directly to the lab and sample water to make the testing solutions. The

addition of aluminum chloride reduced the pH of the testing solution. The pH was brought up, using a sodium hydroxide solution, to between 6.5 and 6.7 for the lab sample or to a pH similar to that of the unspiked water for the site water.

Adding the aluminum salts to test water directly raises additional concerns about floc formation, particularly if solutions aren't aged sufficiently. EPA requests additional information regarding the basis of the decision to add aluminum directly to the lab and sample water to make the testing solutions.

7. Differences between nominal and measured concentrations indicate possible floc issues

Nominal aluminum concentrations were quite a bit higher than measured concentrations for Round 1 and Round 3 tests. Tables 3.4a (laboratory water) and 3.4b (site water) of the WER report are repeated below with the addition of nominal aluminum concentrations for comparison. Large differences in nominal and measured aluminum concentrations may be the result of floc formation.

Table 1. Aluminum concentrations, pH range, and percent survival for *P. promelas* testing in laboratory water (hardness = 10 mg/L). From WER report Table 3.4a (Tetra Tech 2010a) and additional information provided to EPA (Tetra Tech 2010b).

Round	Parameter	Lab							
1	Nominal Al Conc. (mg/L)	0	2.7	5.5	11	22	44	88	175
	Measured Al Conc. (mg/L)	0	1.8	3.0	6.0	11	29	83	112
	pH Range	6.6 - 7.3	6.6 - 7.2	6.5 - 7.2	6.5 - 7.2	6.6 - 7.2	6.7 - 7.2	6.4 - 6.7	6.7
	% Survival	95	50	95	95	55	5	0	0
2	Nominal Al Conc. (mg/L)	0	2.7	5.5	11	22	44	88	175
	Measured Al Conc. (mg/L)	0.02	2.6	5.2	10	20	41	87	166
	pH Range	6.5 - 7.0	6.6 - 7.4	6.5 - 7.2	6.6 - 7.2	6.6 - 7.1	6.6 - 7.0	6.5 - 6.7	6.5 - 6.5
	% Survival	90	95	95	80	95	55	0	0
	Nominal Al Conc. (mg/L)	0	2.7	5.5	11	22	44	88	175
3	Measured Al Conc. (mg/L)	0	1.4	2.6	4.0	5.6	12	34	128
	pH Range	6.6 - 7.0	6.5 - 7.0	6.7 - 7.0	6.7 - 7.0	6.7 - 6.9	6.5 - 6.9	6.5 - 6.5	6.3 - 6.5
	% Survival	100	95	100	90	95	85	0	0

Table 2. Aluminum concentrations, pH range, and percent survival for *P. promelas* testing in site water (hardness = 12 mg/L for Round 1, 16 mg/L for Round 2, and 18 mg/L for Round 3). From WER report Table 3.4b (Tetra Tech 2010) and additional information provided to EPA (see above).

Round	Parameter	Site							
	Nominal Al Conc. (mg/L)	0	2.7	5.5	11	22	44	88	175
	Measured Al Conc.								
1	(mg/L)	0.14	1.4	2.8	5.6	11	22	44	91
		7.0 -	7.0 -	7.0 -	7.0 -	7.0 -	7.0 -	7.0 -	6.8 -
	pH Range	7.2	7.2	7.3	7.3	7.3	7.3	7.2	7.2
	% Survival	95	95	100	95	100	100	90	75
	Nominal Al Conc. (mg/L)	0	5.5	11	22	44	88	175	350
2	Measured Al Conc. (mg/L)	0.08	5.5	11	22	45	89	170	345
		7.0 -	7.1 -	7.2 -	7.1 -	7.0 -	7.0 -	7.0 -	6.9 -
	pH Range	7.4	7.4	7.4	7.3	7.3	7.2	7.1	7.0
	% Survival	95	95	95	90	100	85	10	5
	Nominal Al Conc. (mg/L)	0	11	22	44	88	175	350	700
3	Measured Al Conc. (mg/L)	0.04	11	22	43	86	175	350	675
		6.9 -	7.0 -	6.8 -	6.8 -	7.1 -	6.9 -	6.8 -	6.6 -
	pH Range	7.5	7.5	7.5	7.4	7.3	7.1	7.0	6.7
	% Survival	100	100	100	100	95	90	65	0

During EPA-sponsored studies completed in connection with the aluminum 304(a) criteria revision, floc was formed when the aluminum solution was not aged prior to use. During a 96-hour acute static renewal test with mussels, aluminum hydroxide floc formed in the bottom of test chambers before water renewal on day 2. The test solution was apparently not aged sufficiently, and aluminum had not equilibrated.

For additional acute 96-hour flow through tests for mussels and *Hyalella*, the test solution was held in the tank for a minimum of 24 hours for equilibration before it was used for the test. Aluminum was measured at the bottom and top of test chambers. Very little floc formed in these tests.

Based on the above discussions, EPA recommends that any further aluminum toxicity tests use stock solutions that have been aged for at least 3 hours, preferably longer. In addition, dissolved aluminum in the WER test solutions should be measured every 24 hours, including at the beginning and end of the test and before and after renewal. Acute toxicity tests should follow accepted protocols (ASTM 2014), including the use of a 48-hour duration for cladocerans and a 96-hour duration for fish.

# II. Considerations Related to the Current Aluminum Toxicity Literature

1. Differences Between Proposed Chronic SSC vs Potential EPA Aluminum Chronic Criteria Values

EPA used a preliminary multiple linear regression (MLR) equation to estimate aluminum toxicity and compared the MLR-based criteria to the WER-based SSC. The MLR accounts for effects of pH, hardness, and DOC on the toxicity/bioavailability of aluminum to aquatic organisms. For our evaluation, EPA used the minimum, geometric mean, and maximum values for pH and hardness reported in Table 2 of the technical memorandum *Critical Stream Conditions for Aluminum Toxicity and WER Sampling* (from TetraTech to PacRim Coal, dated 3/16/2106), and the historical levels of DOC reported on page 6 of that memorandum.

EPA found that at all pH, hardness, and DOC combinations, the proposed chronic SSC of  $650 \,\mu\text{g/L}$  exceeds the preliminary chronic aluminum criteria value calculated using the site data. Results are provided in Table 3.

Table 3. Estimated aluminum toxicity at a range of pH, hardness, and TOC levels. Data are based on a preliminary non-peer reviewed multiple linear regression equation and are provided for informational purposes only.

	CCC						
	DOC (min) = 0.8 mg/L						
				рН			
			min	mean	max		
			6.4	7.1	7.9		
ess L)	min	10	47	142	365		
Hardness (mg/L)	mean	22	72	201	408		
На	max	40	99	253	419		
			CCC				
	DOC (mean) = 3 mg/L						
			pН				
			min	mean	max		
			6.4	7.1	7.9		
sss (	min	10	99	160	277		
Hardness (mg/L)	mean	22	140	226	398		
На	max	40	180	318	543		
			CCC				
	D	OC (m	ax) = 6				
			рН				
			min	mean	max		
			6.4	7.1	7.9		
ess L)	min	10	132	167	204		
Hardness (mg/L)	mean	22	191	251	348		
На	max	40	243	325	455		

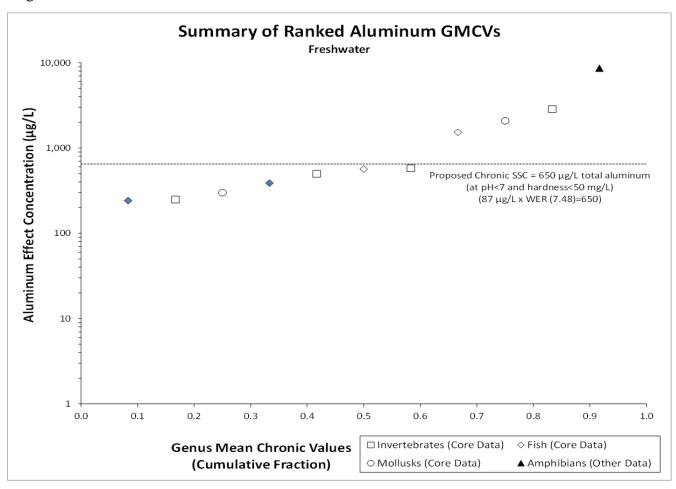
Given that EPA's 304(a) criteria for aluminum are being updated and that a large volume of toxicity data are available now that were not available when the current 304(a) criteria were developed in 1988, and in addition to concerns and considerations described above and in EPA's earlier comments regarding WER toxicity testing procedures and results for aluminum, EPA recommends either the use of a peer-reviewed biotic ligand model or MLR, or adoption of the draft aluminum 304(a) criteria for aquatic life, which EPA expects to publish early in 2017.

2. Comparison of Proposed SSC to Species Sensitivity Distribution (SSD) for Aluminum Toxicity

EPA evaluated the proposed SSC directly against the genus mean chronic values (GMCVs) that have been developed for the current 304(a) criteria update, as shown in

Figure 1. The proposed SSC for Chuitna are also indicated on this figure. GMCV data are normalized to pH 7 and 100 mg/L hardness.

Figure 1.



The following points were noted during this evaluation:

- The draft GMCV for seven of 11 genera is less than the proposed chronic SSC value of  $650 \mu g/L$ .
- Based on current toxicity data used for the 304(a) criterion revision (based on EC20s), 64% of the tested genera would not be protected under the proposed SSC and at a minimum, 20% of an exposed population of a species would experience negative chronic effects such as impaired survival, growth, or reproduction.

- Two genera of the family Salmonidae are included in Figure 1 (indicated by blue shaded diamonds), both among the most sensitive genera:
  - o #1 Brook trout, Salvelinus fontinalis, GMCV = 241.6 μg/L
  - ο #4 Atlantic salmon, Salmo salar, GMCV =  $387.7 \mu g/L$ .

Salmonids are of commercial and recreational importance in the Chuitna system. As indicated in comment A.II.3 on page 4 of EPA's 12/12/2014 comments, sensitive species at the site and downstream of the site should be taken into account in the development of SSC for the Chuitna site.

# III. References

ADEC 2015. Department of Environmental Conservation (DEC) Comment Response, Draft Proposed Site-Specific Criteria and Seasonal Use Revision for Chuit River and Three Tributaries. May 2015.

ASTM 2014. Standard Guide for Conducting Acute Toxicity Tests on Test Materials with Fishes, Macroinvertebrates, and Amphibians. ASTM E729-96(2014). ASTM International, West Conshohocken, PA, 2014. http://dx.doi.org/10.1520/E0729-96R14

EPA 1988. Ambient water quality criteria for aluminum – 1988. EPA 440/5-86-008. EPA Office of water, Washington, DC. August 1988.

EPA 1994. Interim Guidance on Determination and Use of Water-Effect Ratios for Metals. EPA Office of Water, Washington, DC and EPA Office of Research and Development, Duluth, MN and Narragansett, RI. February 1994.

EPA 2015. EPA's Comments on Draft Proposed Site Specific Criteria and Seasonal Use Revision for Chuit River and Three Tributaries. December 12, 2014.

EPA 2016. EPA's Supplemental Comments on Draft Proposed Site Specific Criteria and Seasonal Use Revision for Chuit River and Three Tributaries. March 25, 1015.

Tetra Tech 2010a. Determination of an Aluminum, Copper, Lead, and Zinc Water Effect Ratio for the Chuit River Basin, Alaska. Tetra Tech, Inc., Owings Mills, MD. March 12, 2010.

Tetra Tech 2010b. Email from Henry Latimer, TetraTech, to Bill Beckwith, EPA regarding Chuitna WER questions. May 7, 2010.

Tetra Tech 2016. Critical Stream Conditions for Aluminum Toxicity and WER Sampling. Technical memorandum from TetraTech, Inc. to PacRim Coal. March 16, 2106.





# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION 10

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OFFICE OF WATER AND WATERSHEDS

# **MEMORANDUM**

**SUBJECT:** Variability of Factors that Affect Aluminum Toxicity at the Chuitna Site and

Considerations for WER-Based Site-Specific Criteria Development

**FROM:** Maja Tritt

**TO:** Brock Tabor

Alaska Department of Environmental Conservation

**DATE:** July 21, 2016

#### Introduction

ADEC's 2014 draft decision document for the Chuitna site-specific criteria (SSC) includes a chronic SSC for aluminum that was derived as the geometric mean of three water effect ratio (WER) tests, completed in October and November 2009 using samples collected from station 141. The site to which the SSC was initially intended to apply included Bass, Middle, and Lone Creeks and the Chuitna from the confluence of Bass Creek to its mouth at Cook Inlet. EPA commented that large variability in the individual WER values was observed for the three samples and recommended additional testing to capture the spatial and temporal variability of conditions that affect metals toxicity at the site (EPA 2014, comment II.1). ADEC (2015) responded that the WER studies were completed appropriately and that the variability was a result of different flow conditions. During subsequent calls, Pacific Rim Coal (PRC) cited its 2/27/2014 technical memorandum (Tetra Tech 2014), which presents summary statistics for the site and includes results of an ANOVA to evaluate the variability of aluminum and water quality conditions at the site. This memo is discussed further below.

Following conference calls between ADEC and EPA in 2015 and a request to PRC from ADEC for additional information in response to EPA comments (ADEC 2016), PRC reduced the extent of the site for the aluminum SSC to include only Middle Creek and the Chuitna from Middle Creek to its mouth at Cook Inlet as a means of addressing EPA's concerns about the variability of toxicity-mitigating factors at the site (PRC 2016 and subsequent conversations between ADEC and EPA). ADEC subsequently provided two additional memoranda to EPA regarding the variability of aluminum toxicity factors at the site. The first memo, re: *Critical Stream Conditions for Aluminum Toxicity and WER Sampling* (Tetra Tech 2016a), addresses sensitive conditions at the site, and the second memo, re: *Regression Analysis between Various Parameters* (Tetra Tech 2016b), compares water quality parameters at two sampling locations

within Middle Creek (Stream 2003). The following section provides comments on Tetra Tech (2014), Tetra Tech (2016a), and Tetra Tech (2016b).

PRC provided a database retrieval to EPA on 6/14/2016 that included data for the toxicity-mitigating factors for copper and aluminum as well as flow data. EPA used this data set to complete an evaluation of temporal, spatial, and flow-related variability of factors that may affect aluminum toxicity at the site. This evaluation and recommendations for additional WER testing are also provided below. In response to ADEC's request, EPA completed this evaluation to provide additional guidance to ADEC on the types of technical analyses it could perform to ensure that representative data are collected and used to calculate protective site-specific criteria.

# Review of PRC's 2014 and 2016 Memoranda Regarding Site Uniformity and Sensitive Conditions for Aluminum

PacRim's 2/27/2014 technical memorandum re: *Results of Studies to Establish Site Specific Water Quality Criteria for Aluminum in the Chuit River* (Tetra Tech 2014) includes the stated purpose to "...address questions regarding the representativeness of the ambient source water collected at Station 141 on Middle Creek..." PRC and Tetra Tech discussed this memo during a conference call on 3/21/2016 with ADEC and EPA regarding the draft aluminum SSC and the representativeness of station 141. EPA has reviewed this memo and the two 2016 memos provided by PRC that address the representativeness of the 2009 WER tests and provides comments below. For the purposes of the SSC under consideration, the term "representativeness" refers both to the extent of overlap in the parameters at station 141 versus all others, and importantly to how well Site 141 represents sensitive conditions, i.e., conditions of greatest aluminum toxicity.

In Tetra Tech (2014), PRC concluded that there is no statistical difference in aluminum concentrations across all sites. PRC further concluded that pH, alkalinity, hardness, and conductivity are similar across locations, but no statistical evidence is provided to substantiate this latter claim. PRC presented data in the form of piper diagrams, box and whisker plots, and tables. The main thrust of PRC's argument was based on the apparent spatial similarity in the concentrations of the many chemical parameters measured. From this assessment, PRC concluded that Station 141 is representative of all other sites.

EPA questions the evidence presented by PacRim for the following reasons:

## 1) <u>DOC</u>

Although pH and hardness are important modifiers of aluminum toxicity and data are addressed in Tetra Tech (2014), DOC (or TOC) data are not presented. This omission is a significant oversight, given that DOC plays a large role in aluminum's toxicity. Variability of TOC at the site was addressed in Tetra Tech (2013). Figure 5 of that memo compares TOC in the WER samples with TOC in Middle Creek (Stream 2003) and shows that the low end of the TOC range in Middle Creek was not captured by the WER tests. TOC in the third WER test, which had the lowest TOC levels, was slightly below the average TOC concentration at the two Middle Creek monitoring locations.

# 2) Spatial and Temporal Representativeness

Spatial representativeness is assessed in the document via an aggregation of data by 'site', apparently irrespective of sample date and time. After data were aggregated according to sampling site, box and whisker plots were used to provide an idea of the overlap between sites for several parameters including pH and hardness. The argument was then made that these data plots indicate a lack of spatial dependence of the results (i.e., it is inferred that all sites had statistically equivalent parameter values). No statistical tests were performed for this important assessment, which is problematic given the importance of these parameters on the toxicity of aluminum. It is not clear if station 141 is different or the same for any parameter, given the lack of statistical testing and consequent reliance on visual interpretation of the plots.

Secondly, an ANOVA was used to statistically test for a difference in aluminum concentrations by site. Note that ANOVA can only be used for data that are normally distributed and homoscedastic (a Welch ANOVA can be used for data that are normal but heteroscedastic). If data are not normally distributed, a transformation may be required, or the use of a non-parametric test would be warranted. Tetra Tech (2014) presents no information on the validity of conducting an ANOVA on aluminum concentrations. Oftentimes, chemical concentrations in the environment are lognormally distributed, suggesting the need to at least include information that supports the use of ANOVA. For these reasons, based on information provided in Tetra Tech (2014), EPA is not able to conclude that waters at location 141 contained the same or different parameter concentrations as waters across the site.

Several documents provided by PRC indicate that in general parameters can vary with year (Tetra Tech 2013) and within a year (Tetra Tech 2016a,b). However, it is not sufficiently clear during which season(s) the most sensitive conditions occur within the Chuitna watershed. Given that temporal variation is not well characterized, the aggregation of data as in Tetra Tech (2014) appears to be unwarranted. Spring and sometimes autumn appear to be times when the region reaches sensitive conditions (details are provided below), but data aggregation obscures that variability for each site. It is not possible to determine where and when the most sensitive conditions are reached across the site based on the data presentations provided in the memos.

#### 3) Sensitive conditions:

Because few WER tests have been conducted and the results exhibited significant variability, an analysis is needed that clearly demonstrates parameter variation across both space and time to ensure that sensitive conditions have been examined in WER testing. Given the issues stated above, it is not clear from the information provided by PRC whether station 141 represents other locations in pH, hardness, or DOC levels. Further, it is not clear whether station 141 or any other location captured the most sensitive annual conditions. Because of this ambiguity, it is not clear which conditions the WER tests represented.

EPA appreciates the effort taken to generate statistical support for the correlation between parameters key to aluminum's toxicity and thus to determine if other sampling periods would detect the most sensitive conditions (Tetra Tech 2016b). However, EPA does not concur with the

selected method. The variables do not appear to be linearly related, but a lack of a linear relationship is not evidence for the absence of a relationship between parameters. EPA has conducted an analysis of parameter variability across space, time and flow rates and provides that information below. EPA recommends the use of an approach such as this to characterize the variability of toxicity parameters and identify sensitive conditions at the site for further development of protective SSC.

With respect to the memo dated March 16, 2016 (Tetra Tech 2016a), EPA refers ADEC to our previous memo concerning the validity of the WER test procedures (EPA 2016). Given the small difference in water chemistry between the three WER samples, it is likely that test conditions and floc formation played a role in the observed variability in the WER tests, particularly test 3. While not documented in the WER report, the presence of floc would call the validity of the toxicity test into question.

Regarding the representativeness of the WER tests to sensitive conditions, EPA concurs with PRC that the low pH and hardness values captured by the WER tests may have reflected some of the more sensitive conditions found at station 141 (but see Table 1); however, DOC levels in the WER samples do not adequately represent sensitive conditions at the site (Table 1). Based on EPA's analysis of data provided by PRC, DOC levels appeared to be at their lowest in the spring, along with pH and hardness reductions during high flows (analysis provided below). The March 16, 2016 memo (Tetra Tech 2016a) acknowledges that the lower TOC levels at station 141 were not captured and provides the justification that "the values observed during testing were typical of conditions in this system." However, SSC must protect the site as a whole (EPA 1994), and the aquatic life SSC for the Chuitna site must therefore be protective during sensitive conditions as well as typical conditions.

# Assessment of Variation of Aluminum Toxicity Factors Spatially, Temporally, and with Flow

Because aluminum toxicity is known to vary with pH, DOC, and hardness and these parameters vary across space and time in the environment, it is important to characterize the nature of this variation at the SSC site in order to guide future water sampling for WER testing. Therefore, EPA statistically analyzed PRC's historic water quality data from the Chuitna watershed for spatial and temporal variability and variability with stream flow. These data included 28 unique parameters measured over a time span of 28 years and across 11 monitoring stations. Stream flows were also included. EPA combined data from stations 140 and 141 and stations 195 and 196 (see Rti 2009, section 3.2), making for a total of nine unique sampling locations. Because aluminum toxicity is primarily affected by pH, DOC, and hardness, EPA focused its analysis on these three parameters. The large size of the dataset allowed EPA to view patterns that would not have been observable with a small dataset, i.e., a data set that only included the sampling locations within the current aluminum SSC site. Following the global assessment of patterns, stations 140/141 (Middle Creek) and 230 (Chuitna) were separately examined to determine if the global patterns also occurred on the more local level.

The analytical approach was as follows:

- Selected the data subset as indicated above.
- Assessed spatial variation of each of the three parameters by pooling data by station.

- O Data were graphed as mean±SEM (standard error of the mean) for each parameter by station ID. Means and standard errors were plotted only to simplify viewing, not to interpret statistical significance.
- Executed Kruskall-Wallis statistical test in Statistica (version 10) to determine if parameter values were statistically different across stations. The Kruskall-Wallis test is a non-parametric alternative to ANOVA based on ranks to compare three or more groups (e.g., stations or months) for the same median when no data distribution is assumed.
- Assessed temporal variation of each of the three parameters by pooling data by month.
  - o Data were graphed as mean±SEM for each parameter by month.
  - Executed Kruskall-Wallis statistical test to determine if parameter values were statistically different across months.

This above analytical process provided evidence for the following trends:

#### • Field pH:

- o Figure 1 shows variation of pH by month and station. Note that the small panel within figure 1 shows pH trends without September 2007 data. We removed these data for that figure panel because they appeared to be aberrantly low, perhaps due to analytical error. With or without these data, the sampling recommendations are similar.
- o pH varied by month and station ID with P < 0.05.
- o pH was lowest in May and June and secondarily in September and October (excluding the aberrantly low September 2007 data).
- o pH was lowest at station 140/141.
- o Flow and pH did appear to negatively correlate, suggesting that increasing flows may provide an indicator of sensitive conditions (low pH). Therefore, it is important to sample during peak flow periods to capture sensitive pH conditions.

#### • Total hardness as CaCO<sub>3</sub>:

- o Figure 2 shows variation of hardness by month and station.
- o Hardness varied by month (P<0.05) but not by station ID (P>0.05).
- o Hardness was lowest in May, June, and September.
- o Hardness may have been lowest at station 45, but no statistics were performed for this finding because the Kruskall-Wallis statistic was not significant.
- o Flow and hardness did appear to negatively correlate, suggesting that increasing flows may provide an indicator of sensitive conditions (low hardness).
- Therefore, it is important to sample during peak flow periods in order to capture sensitive (low) hardness conditions.

#### • TOC:

- o Figure 3 shows variation of TOC by month and station.
- o TOC concentration varied by month and station ID with P < 0.05.
- O TOC concentration was lowest during what is presumed to be the cold weather months of December through March and increased after that until peaking in September. No TOC data were available in the data set for October and November. However, TOC levels in the WER samples were high in early October but decreased from October to November, with concentrations at 7.7, 6.2, and 4.5 mg/L on 10/4, 10/25, and 11/29/2009 (Tetra Tech 2010, p. 16). This decreasing pattern in late fall is consistent with the observed temporal trends at the site for TOC.
- TOC concentration appeared to be lowest at stations 230 and 45 and highest at station 129. TOC concentrations at station 141 were in the moderate range relative to other locations.
- o Flow and TOC did not appear to be correlated.
- o Therefore, it is important to sample during the early spring, irrespective of stream flow, in order to capture sensitive (low) TOC (and DOC) conditions.
- See Figure 4 for a visual representation of how flow varied with TOC, pH and hardness on a monthly basis.
- WER testing from 2009 did not encompass the more sensitive conditions at the site for any of the three parameters (see Table 1).

### Additional WER Testing Likely to Capture Sensitive Conditions at the Site

In order to be protective overall, SSC must be sufficiently stringent to protect the more sensitive conditions at the site, i.e., conditions of greater aluminum toxicity. Taken together, the above data trends suggest that further WER testing is needed in order to capture conditions at the site that would be predicted to result in the greatest aluminum toxicity. EPA provides the following recommended approach for additional WER testing that is likely to result in the successful capture of sensitive conditions.

Spring high flow conditions appeared to exhibit simultaneously low TOC, pH and hardness levels, while fall high flow conditions exhibited low pH and hardness. However, because 1) the existing data do not fully characterize the variation of these water quality parameters, and 2) toxicity is not solely dependent on these three parameters, as a conservative approach, EPA recommends completing WER tests in each water body to which the SSC will apply and during peak flows of spring and fall, in order to be more confident of capturing sensitive conditions for WER testing. EPA has essentially stratified the data in order to focus its sampling recommendations on what current knowledge suggests is most predictive of the greatest aluminum toxicity, but EPA is open to other sampling options that improve upon this approach in terms of capturing the most sensitive conditions at the site.

In summary, given the above findings and that aluminum bioavailability is influenced by pH and, to a lesser extent, DOC and hardness, and that WER testing must represent sensitive conditions, EPA suggests the following approach to collecting WER samples that successfully capture the more sensitive conditions at the site:

- Sample peak flow conditions at stations 140/141 (Middle Creek) and 230 (Chuitna) during spring snow melt (May-June) and late summer rains (August-September).
  - These locations encompass the proposed SSC site and appear to exhibit different toxicity parameter values.
  - O These months appear to reflect simultaneously low values for at least two of three parameters of toxicity. May-June (high flows) is an especially critical period given concurrent lower TOC, pH, and hardness. August-September provides a second period with at least concurrently low pH and hardness.
- Consider tracking real-time flow data to guide real-time water quality monitoring for pH and hardness (using a YSI probe or similar instrumentation). Real-time measurement of hardness is preferable, but because conductivity and flow were negatively correlated as were hardness and flow, conductivity appeared to provide an index of low hardness. Thus, real-time measurements of conductivity could be used as a way to track changes in hardness and other parameters that fall with rising flow.
- As flow rises, water quality parameters are expected to fall, indicating a good time to start regular real-time monitoring.
- If possible, conduct toxicity test for each sampling location and season with water collected during rising limb, peak, and falling limb, ensuring that at a period of least three weeks separates each test, for a total of three tests over approximately 6 weeks as specified in EPA (1994).
- Ensure that toxicity tests occur when pH and DOC and hardness are near their low percentile historic concentrations to ensure that sensitive conditions are captured in WER toxicity tests (see Table 1 for summarized historic data).

As stated earlier, additional WER sampling is necessary to capture sensitive conditions at the site and ensure that SSC are protective overall. The above approach represents a scenario that provides a high likelihood of capturing sensitive conditions. EPA looks forward to further discussions with ADEC and PRC to develop a detailed approach for additional WER testing, if further WER tests are pursued as a basis for developing SSC, including temporospatial and flow considerations provided in this memo and considerations related to best practices for aluminum toxicity testing procedures (EPA 2016).

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<sup>&</sup>lt;sup>1</sup> Hardness may be estimated using a field measurement if available, but it must be measured in the lab for any toxicity test following standard procedures in the QAPP.

**Table 1**. Range and 10<sup>th</sup> percentile values for the three parameters most influencing aluminum bioavailability as compared to parameter values in WER tests.

Parameter	WER	140/141	230	SSC site
рН	6.7-7.3	6.2-7.9 (10 <sup>th</sup> , 6.6)	6.1-8.0 (10 <sup>th</sup> , 6.6)	6.1-8.6 (10 <sup>th</sup> , 6.7)
TOC	4.5-7.7	2.0-8.0 (10 <sup>th</sup> , 2.0)	1.0-4.0 (10 <sup>th</sup> , 1.0)	1.0-24.0 (10 <sup>th</sup> , 2.0)
Hardness	12.0-18.0	10-40 (10 <sup>th</sup> , 10.0)	10-30.0 (10 <sup>th</sup> , 10.0)	10.0-40.0 (10 <sup>th</sup> , 10.0)

Figure 1. pH variation across month (A) and station (B), and with September 2007 data removed (C).

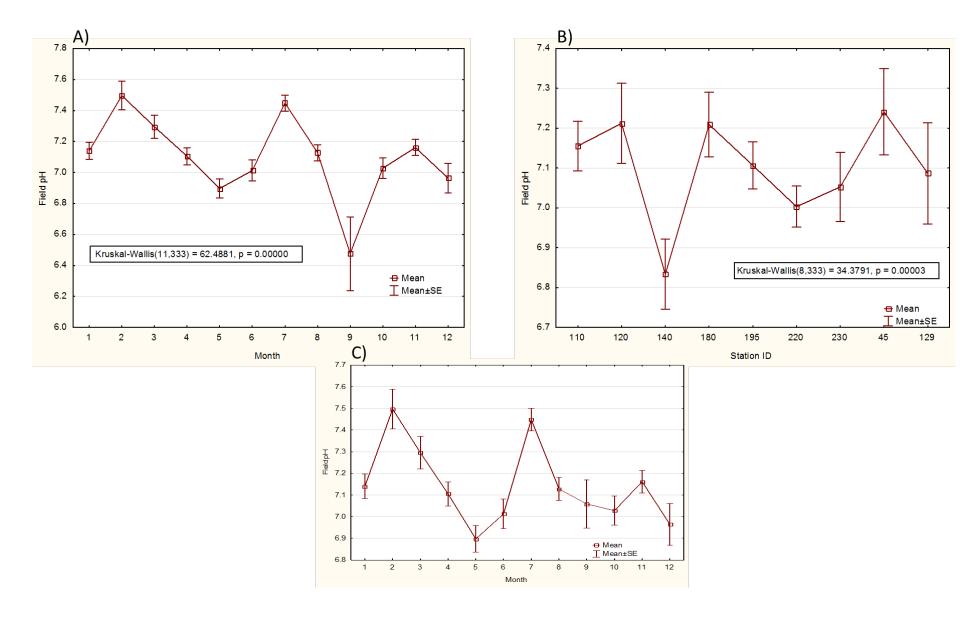
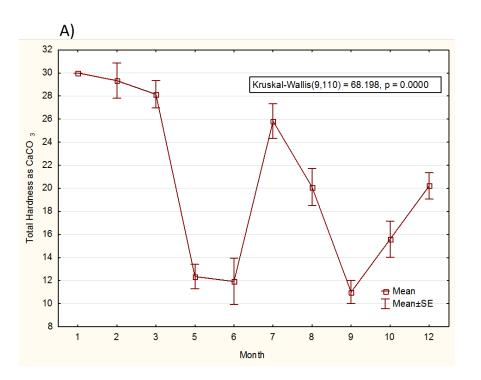


Figure 2. Hardness variation across month (A) and station (B).



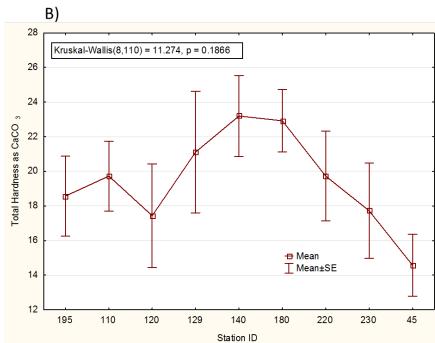
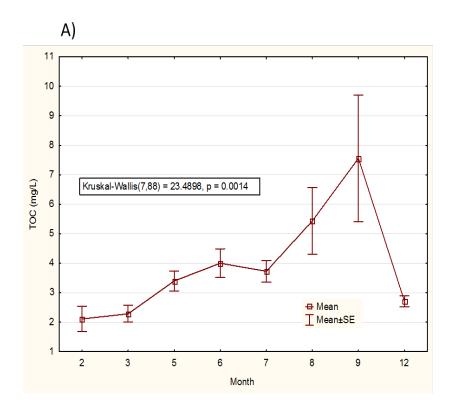


Figure 3. TOC variation across month (A) and station (B).



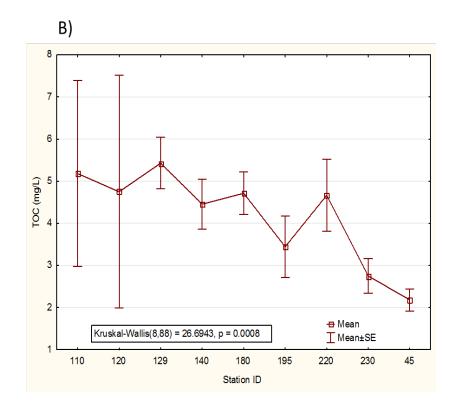
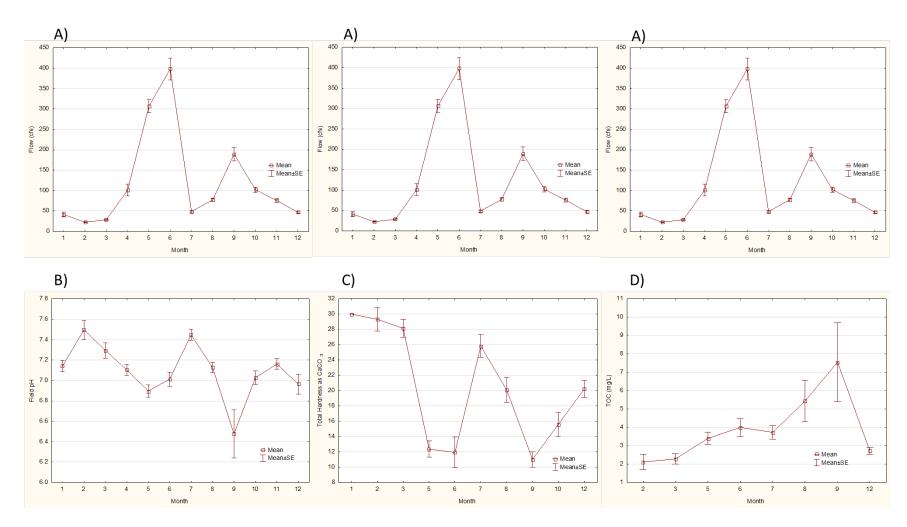


Figure 4. Variation in stream flow (A), pH (B), hardness (C), and TOC (D) by month.



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